

## Description

# [METHODS FOR THE PRODUCTION OF MARBLE-LIKE CRYSTALLIZED GLASS PANEL WITH EMBOSSED SURFACE]

### CROSS REFERENCE TO RELATED APPLICATIONS

- [0001] U.S.3,554,72501/1971Bracken et al.  
G.B.142779201/1972Nippon Electric Glass  
U.S.3,672,85906/1972Claussen  
U.S.3,843,34310/1974Okada et al.  
U.S.3,955,98905/1976Nakamura  
U.S.4,054,43510/1977Sakane et al.  
U.S.4,746,34705/1988Sensi  
U.S.5,089,34502/1992Hashibe et al.  
U.S.5,403,66404/1995Kurahashi et al.  
U.S.5,885,31503/1999Fredholm et al.

### BACKGROUND OF INVENTION

- [0002] This invention relates to the process of producing flat crystallized glass panel with embossed surface which re-

sults stereoscopic aspect and better static friction on the surface to prevent from slipping under wet condition, so it can better be used on floor application and others.

[0003] *DISCUSSION OF PRIOR ART*

[0004] Crystallized glass has been utilized in the manufacturing of such varied articles as cookware, tableware, missile nose cones, protective shields, and in the computer and electronics field. Nowadays, crystallized glass has been used as ornamental building materials to replace the natural stones due to its excellent characteristics in mechanical strength, heat-resistance, chemical corrosion strength, and water resistance, and has obtained great popularity. However, its glossy and smooth surface together with its pure color often creates simple and cold environmental feelings. Several patents (G.B. 1427792, 1972; U.S. 3,843,343, 1974, Okada et al.; U.S. 3,955,989, 1976, Nakamura; U.S. 5,403,664, 1995, Kurahashi et al.) disclose the methods of producing surface pattern over crystallized glass flat panel. However, these methods are limited in changing the color pattern of the surface rather than the roughness of the surface. As a result, the crystallized glass has inherited the smooth and glossy characteristic of glass and has limited its use from floor applica-

tion due to the potential risk of slip.

[0005] The U.S. Patent 5,089,345, 1992, Hashibe et al. states that it is uneconomical to apply molds with rough and uneven surface to produce crystallized glass with uneven surface, and discloses a method of producing crystallized glass with an irregular rough surface pattern. However, the rough surface is produced by overlapping flaky and flattened crystallized pieces at "random" at the bottom of the glass article. The resulted surface is therefore unpredictable.

[0006] Many U.S. Patents (U.S. 3,554,725, 1971, Bracken et al.; U.S. 3,672,859, 1972, Classen; U.S. 4,746,347, 1988, Sensi; U.S. 5,885,315, 1999, Fredholm et al.) disclose methods of using molten glass to form glass sheets with rough surface patterns through mechanical rollers. However, the process is not adequate for producing marble-like crystallized glass.

[0007] *OBJECTS AND ADVANTAGES*

[0008] The main objective of the present invention relates to marble-like crystallized glass articles is to provide methods to produce a regular or irregular embossed surface.

[0009] The present invention that produces crystallized glass with regular or irregular embossed surfaces can increase

the static friction of its surface over 20%, comparing to the traditional smooth surface, to better prevent from slipping under wet conditions.

- [0010] The present invention that produces crystallized glass with regular or irregular embossed surface can create a stereoscopic aspect with less mirror-like light reflection to provide better visual comfort.
- [0011] The present invention that produces crystallized glass with regular or irregular embossed surface has uniform, predictable and consistent surface pattern.
- [0012] The present invention requires no additional tools. It is accomplished by controlling the crystallizing temperature profile and the Molding procedures over various sizes of glass particles.
- [0013] The present invention is cost effective and economically ideal for mass production.

#### **SUMMARY OF INVENTION**

- [0014] The crystallized glass is an ideal substitution of natural stone as ornamental building materials because of its superior mechanical strength, heat resistance, and efflorescence resistance. In general, all flat or curved crystallized glass articles have glossy and smooth surface, and therefore have very limited application on floor due to the po-

tential risk of slip.

[0015] Crystallizable glass can be obtained by heating the special formulated, mixed raw materials of glass at a temperature of over 1400°C. The molten glass is water granulated into glass granules. During the crystallizing process, glass granules are softened, deformed and fusion-bonded together along their interfaces. Along with the desired temperature profile, the  $\beta$ -type needle-like crystals are formed from the surface of the glass granules toward the interior (crystallization). In completion of the crystallization, the integral crystallized glass article is obtained (G.B. 1427792, 1972; U.S. 3,843,343, 1974, Okada et al.; U.S. 3,955,989, 1976, Nakamura; U.S. 4,054,435, 1977, Sakane et al.; U.S. 5,403,664, 1995, Kurahashi et al.).

[0016] The present invention relates to a process of producing crystallized glass, requires no special molds, consists of six general steps:

[0017] (1) *Molten glass materials*: Crystallizable glass of the systems  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$  or  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--ZnO}$ , or others may be employed. The formulated glass materials are heated at 1400–1600°C.

[0018] (2) *Water granulation*: The molten glass (1) is granulated in water into glass particles with less than 10 mm in size.

The ideal water temperature is around 40–60°C. The granulated glass particles are collected and dried.

[0019] (3) *Molding*: The granulated glass particles are loaded on a flat refractory mold with surrounding frames. The top surface of the mold and interior surfaces of the frames are coated with a mold release agent ( $\text{Al}_2\text{O}_3$  powder or others).

[0020] (4) *Crystallizing*: During heat-treated process, glass granules are softened, deformed and fusion-bonded together along their interfaces. Along with the desired temperature profile, the  $\beta$ -type needle-like crystals are formed from the surface of the glass granules toward the interior (crystallization). In completion of the crystallizing process, the integral crystallized glass article is obtained.

[0021] (5) *Flow deformation*: At liquefied temperature, the flow deformation is formed and advanced on the surface of glass article to fill up the space among glass particles to produce a smooth and even surface.

[0022] (6) *Cooling*: A proper temperature profile is applied for cooling, so the glass article will not crack or distort.

[0023] The original crystallized glass articles and natural stone, such as marble or granite, have a polished, smooth, and glossy surface. The present invention is to produce the

crystallized glass with embossed surface. It creates a stereoscopic aspect over the surface for better visual comfort and increases static friction to prevent from slipping under wet conditions. The invention requires no additional tools but various process techniques. It is cost effective and easy to be adopted for mass production.

[0024] It is possible to produce a rough surface of the glass articles by overlapping crystallizable glass pieces at the bottom of the mold and uses it as principal surface (ref Patent U.S. 5,089,345). However, the surface condition is hard to predict and is not adequate for mass production.

[0025] The present invention provides two different methods in producing crystallized glass with an embossed or uneven surface.

[0026] Method 1: to control the flow deformation process to obtain the embossed surface (FIG. 1a – 1c).

[0027] Method 2: to load the glass particles with both glass bits and pieces to create the variation of the density of the glass body, so as to produce an uneven surface (FIG. 2a 2f).

## **BRIEF DESCRIPTION OF DRAWINGS**

[0028] FIG 1a illustrates that the glass body is prepared by loading various sizes of glass particles into the mold and

ready for crystallization process.

[0029] FIG 1b illustrates that the flow deformation smoothes the surface.

[0030] FIG 1c illustrates that to control the flow deformation in effect creates a non-smoothed surface.

[0031] FIG 2a & 2b are diagrams that illustrate the thickness of glass body before and after the crystallization process.

[0032] FIG 2c & 2d are diagrams that illustrate the thickness of glass body, before and after crystallization process, which mixes the glass bits with flat glass pieces together.

[0033] FIG 2e illustrates the method of loading the glass particles with both glass bits and glass pieces.

[0034] FIG 2f illustrates the result of the crystallized glass panel with an uneven surface of 2e.

#### **DETAILED DESCRIPTION**

[0035] Method 1: The crystallized glass articles are commonly produced with a smoothed surface. The crystallizing process requires the glass body to be at a temperature where the flow deformation is advanced in order for the surface to be totally smoothed out. It is suggested in the previous patents (ref. Patents G.B. 1427792, U.S. 3,843,343, U.S. 3,955,989, U.S. 4,054,435) that to keep the glass body at about 1150°C for one hour to complete the crystallizing



and flow deformation processes. It is our invention to control the flow deformation process, so the spaces among glass particles are filled with glass flow, but the glass particles are not completely flattened down. To do so, we divide the procedure into two steps as follows:

[0036] 1) keep the glass body at a temperature lower than the temperature that the flow deformation process needs (about 20°C below) for a period of time, then

[0037] 2) raise up the temperature to where the flow deformation process requires for time as needed.

[0038] The first step of process provides enough time for the crystals to grow within the glass body. It also prepares the glass body in temperature close to the flow deformation process needs, so the flow can happen quickly as soon as the temperature rises. In step two, we control the time factor of the process to obtain the desired surface condition as we needed. It is important to know that the formula of glass, the size of the glass particles, the type of furnace used, and the required deviation in depth over the surface are all important factors in determining those temperature and time parameters. The basic procedure is as follows:

[0039] 1.To prepare crystallizable glass bits with size of 10 mm

or less.

[0040] 2. Apply mold release agent over the refractory mold and frames to prevent the glass from adhering on the mold during the crystallization.

[0041] 3. Putting the glass bits in 1) into the mold over the mold release agent and leveling the surface.

[0042] 4. Place the mold into furnace for heat-treatment.

[0043] 5. In conjunction with the crystallizing process, kept the glass body at about 20°C below the temperature of flow deformation process for a period of time, so the crystals are formed inside the glass bits and the glass bits are all fusion-bonded together

[0044] 6. Kept the glass body at the temperature where the flow deformation process requires for a period of time as desired.

[0045] 7. Polishing the surface as desired and to remove sharp bumps.

[0046] Method 2: The thickness of the crystallized glass article is usually about 40% 60% (depends upon the size of particles) of the height of the glass body before it is crystallized, This is due to the fact that different size of glass particles, after fusion bonded together, produces different porous body, and therefore results different density of the

article (ref Patent U.S. 4,054,435). On the other hand, the density of the glass body varies the thickness of the glass article. It is our invention to load the glass body with different glass particles, so it has different density in different locations among the glass body. Controlling the time of flow deformation process can produce crystallized glass panel with un-even surface. The basic procedure is as follows:

- [0047] 1.To prepare crystallizable glass bits with size of 5 mm or less.
- [0048] 2.To prepare flat crystallizable/crystallized glass pieces with thickness and shapes desired (circle, square, hex, etc...).
- [0049] 3.Apply mold release agent over the refractory mold and frames to prevent the glass from adhering on the mold during the crystallization.
- [0050] 4.Place the flat glass pieces prepared in 2) on the mold over the mold release agent in position desired.
- [0051] 5.Fill up the mold with glass bits prepared in 1). The glass bits may/may not cover the surface of the glass pieces.
- [0052] 6.Place the mold into furnace for heat-treatment.
- [0053] 7.In conjunction with the crystallizing process, kept the glass body at about 20°C below the temperature of flow

deformation process for a period of time, so the crystals are formed inside the glass bits and the glass bits are all fusion-bonded together

[0054] 8. Kept the glass body at the temperature where the flow deformation process requires for a period of time or as desired.

[0055] 9. Polishing the surface for desired finishing.

[0056] *EXAMPLES*

[0057] The crystallizable glass bits used is within  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-ZnO}$ . The size of the mold is around 1000mm x 1000mm. The refractory mold is coated with  $\text{Al}_2\text{O}_3$  to prevent the glass from adhering on the mold during the crystallization.

[0058] Example 1,

[0059] Two sizes of crystallizable glass bits are used, one with size between 3–5 mm (type A) and another with size 3 mm or less (type B). Load 25kg glass bits of type B into the mold over the mold release agent and level the surface. Load another 25kg glass bits of type A into mold over the glass bits previously loaded. Leveling the surface. Place the mold into furnace and follow its regular temperature profile for heat-treatment. Maintain the temperature

to 1115°C for 40 minutes. The crystals are then formed inside the glass bits and the glass bits are all fusion-bonded together. Maintain the temperature to 1135°C for 30 minutes. In completion of cooling process, polish the surface as desired. The polished article has craters on surface uniformly with average size > 5 mm and depth of 0.2 0.5 mm.

[0060] Example 2,

[0061] The crystallizable glass bits with size of 3 mm or less and flat crystallized glass pieces with size of 30mm x 30mm and thickness of 3mm are used. The flat glass pieces are placed on the mold over the mold release agent with 100 mm apart. Load 50kg glass bits into the mold over flat glass pieces and level the surface. Place the mold into furnace and follow its regular temperature profile for heat-treatment. Maintain the temperature to 1115°C for 40 minutes. The crystals are then formed inside the glass bits and the glass bits are all fusion-bonded together. Maintain the temperature to 1135°C for 30 minutes. In completion of cooling process, polish the surface as desired. The polished article has square shaped bumps on surface uniformly with average size < 30 mm and depth <1.2 mm.